

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION Mastic Tile Resin

5 We, PENNSYLVANIA INDUSTRIAL CHEMICAL CORPORATION, a corporation of the State of Pennsylvania, United States of America, of Clairton, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to tile resins and tile binders especially adapted for use in the production of mastic, or asphalt, tile.

15 In the production of asphalt some of the specifications, such as those of Federal Specification SS-T-306b may be met without great difficulty. It has generally been true, however, that it is with some difficulty that mastic tile satisfactorily and economically meets the specifications for resistance to vegetable oils, 20 such as cottonseed or lard oils, to kerosene, and to mild alkalis, such as trisodiumphosphate solution created by, for example, the Asphalt Tile Institute.

25 The resins available heretofore for use as binders for mastic tile have not been entirely satisfactory in the latter connection. Polystyrene base binders have good color and good color stability but they do not achieve the desired grease resistance. Modified 30 phenolic resins, such as the modified phenolic-maleic resins, do give a satisfactory degree of grease resistance but they still lack desired resistance to light, and the colors of the finished tile are often not as bright as desired. 35 In the past blown and bodied oils have been used with hydrocarbon resins to produce tile having satisfactory grease resistance but they show inadequate resistance to alkali.

40 With further reference to hydrocarbon resins, when plasticized to supply tile binders some exhibit excellent resistance to kerosene but in general they are high melting, and when sufficient plasticizer has been added to give a tile that is satisfactory, for instance 45 with respect to indentation, the grease resist-

ance does not meet accepted standards.

Partly because of such deficiencies of the previous tile resins and binder compositions of them with plasticizers, especially with respect to the development of greaseproof asphalt tile, this type of mastic floor covering has not up to this time achieved the commercial acceptance that would normally have been expected due, largely, to the unavailability of a reasonably inexpensive binder capable of producing a tile that is satisfactorily greaseproof and alkali resistant. 55

It is among the objects of this invention to provide tile resins and plasticized binders thereof productive of mastic tile that meet standard specifications for resistance to mineral and vegetable oils and to alkali; that are adapted likewise to the production of tiles of bright color, and that possess other tile binder desiderata, such as color stability under exposure to light. 65

It is among other objects of the invention to provide tile resins, and binders compounded therefrom, for the production of asphalt tile comprising, in addition to thermoplastic binder, fibrous material, such as asbestos, filler, such as limestone, and pigment, that are characterized by meeting the specifications for grease and alkali resistance of the Asphalt Tile Institute; that may be plasticized with readily available substances; that may, if desired, be used as extenders for vinyl resin binders; and that are readily produced from available materials and are attractively inexpensive. 70

The present invention provides a resin composition for mastic tile comprising a blend of a copolymer of a major proportion of styrene and a minor proportion of acrylonitrile, acrylamide or methyl vinyl ketone, and a substantially non-volatile plasticizer said resin having a melting point of from 70° to 110°C. 75

The invention also provides mastic tile of good colour stability and grease resistance, 80 90

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which comprises fibrous material, filler, pigment, and a thermoplastic binder, said thermoplastic binder comprising a blend of a copolymer of a major proportion of styrene and a minor proportion of acrylonitrile, acrylamide or methyl vinyl ketone, and a substantially non-volatile plasticizer, and said thermoplastic binder having a melting point of from 70° to 110°C.

In the case of acrylonitrile, we have found that less than 5 per cent of it in the copolymer results in a resin and tile binder that gives tile of inadequate grease resistance. We have found also that there is no advantage in having more than 10 per cent of acrylonitrile in the copolymer with styrene.

The copolymers of this invention may be made by procedures familiar to those concerned with the production of polymers, examples of which will appear hereinafter.

The copolymers employed in this invention may be blended with a variety of plasticizers, such as those commonly used with vinyl chloride resins including, for instance, di-octyl phthalate and tri-cresyl phosphate, to give a resin having a melting point of from 100° to 110°C. Such blends may then be softened further (as to 70°C) to produce tile binders for making greaseproof tile. For the latter purpose a particularly useful softener is supplied by polymerizing styrene with clay and stripping the product to a resin of about 25°C melting point; such a product is available on the market as Piccolastic A-25 (a soft styrene polymer), or Aromatic Plasticizer 25 (a resin formed from the condensation of olefins with aromatic hydrocarbons and having a softening point of about 25°C and an aniline point of about 50°C), which latter has a high degree of aromaticity that adapts it particularly to the plasticizing of the copolymers of this invention, and it contributes to the production of mastic tile of excellent light stability. For some purposes, as where optimum resistance is not requisite, Piccolastic A-25 or other highly aromatic hydrocarbon plasticizer may be replaced in part by coumarone-indene or other hydrocarbon resins of 60° to 100°C softening point. Other substantially non-volatile plasticizers useful in the practice of the invention are described in connection with the following examples.

The tile resins of this invention may be used in the production of mastic tile according to conventional and well known procedures. Such tile are, broadly considered, constituted of fibrous materials, such as asbestos fiber, fillers, such as limestone, pigments and thermoplastic binder.

#### Example 1.

A mixture of 94 parts by weight of 99.6 per cent styrene and 6 parts of acrylonitrile was added during 4 hours to an equal weight of Hi Solv 471 oil heated, as solvent, to 160° to

165°C, following which the mixture was refluxed at 165°C for 44 hours. The product was then steam stripped to remove the solvent and any unreacted monomers, resulting in a yield of 99 per cent of copolymer resin based on the monomers. This copolymer had a melting point of 141°C. It contained 5.4 per cent of acrylonitrile based upon the nitrogen content as determined by the Kjeldahl method. 70 parts of this copolymer was blended with 24 parts of Atlantic 14 Oil, a naphthenic mineral oil, and 6 parts of limed tall oil pitch, as plasticizers, to form tile binder of about 80°C melting point. Tile made from it gave an initial, or blank scratch of 0.062 by the Taber scratch test of the Asphalt Tile Institute specification for grease resistance asphalt tile. After exposure during 24 hours to kerosene, cottonseed oil and trisodiumphosphate solution in accordance with those specifications the tiles showed, respectively, 0.076, 0.076 and 0.068 scratch width. Thus the tile made from this binder admirably meet the specifications for grease resistance and alkali resistance since the specification allows double the blank scratch width on the Taber test. It may be noted that it is not considered in the trade good practice to market tile with scratch widths that are close to the specification limit, thus showing the desirable nature of the copolymer binders of this invention. The tile likewise showed an initial penetration of but 7.1 mils.

#### Example 2.

In this instance 93 parts of 99 per cent styrene and 7 parts of acrylonitrile were refluxed at 165°C for 44 hours. The copolymer produced had a melting point of 136°C. It was then blended with 20 per cent by weight of Hercolyn, a hydrogenated methyl abietate, 30 parts of Picco T-100 (a resin made by polymerization with acid catalysts of unsaturated petroleum distillates), and 8 parts of HSD oil (a heavy aromatic oil) as plasticizers to produce a binder of 108°C melting point which was then milled and further milled with 15 parts of di-octylphthalate to produce a final binder having a softening point of about 80°C. Tile produced from this binder had entirely satisfactory resistance to kerosene, cottonseed oil and Na<sub>3</sub>PO<sub>4</sub>.

#### Example 3.

90 parts of 99 per cent styrene and 10 parts of acrylonitrile mixed with an equal weight of Hi Solv 30 (a petroleum aromatic solvent boiling in the range 130° to 180°C) were heated at 165°C during 48 hours to produce a resin copolymer of 142°C melting point. The copolymer was then blended and plasticized with 30 per cent by weight of Piccolastic A-25 and 20 per cent of Aromatic Plasticizer 25 (a resin formed by the condensation of olefins with aromatic hydrocarbons and having a softening point of about 25°C and

an aniline point of about 50°C). This blend melted at about 110°C. It was further plasticized with 17 per cent of di-octylphthalate to form a tile binder having a softening point of about 79°C, and when this binder was mixed with limestone, asbestos fiber and pigments there was produced a tile meeting the grease resistance specifications and having excellent stability to light and good resistance to indentation.

#### Example 4.

93 parts of monomeric styrene (99.6 per cent purity) and 7 parts of acrylonitrile were refluxed in Hi Solv 30 (an aromatic hydrocarbon solvent boiling at 130° to 180°C) for 48 hours at 138° to 145°C. This copolymer was finished by steaming, and had a melting point of approximately 160°C. When blended, using 52 per cent of the 93-7 copolymer with 35 per cent by weight of 25°C melting point coal tar resin (of the coumarone-indene type), and 13 parts by weight of Atlantic No. 14 (naphthenic mineral oil) as plasticizers, a tile resin of 108°C softening point was obtained. This resin was blended and further plasticized with Atlantic No. 14 and lined tall oil, to give a 70°C melting point binder, which was blended with a filler, consisting of 40 parts of 7-R Asbestos, 55 parts of ground limestone, and 5 parts of pigments, using 23 parts binder and 77 parts filler to give a tile having an initial penetration of 9, and penetration at 115°C of 15. The control Taber abrasion of this material was 0.60; the kerosene resistance was 0.070; the cottonseed resistance was 0.086; the trisodium sulphate resistance was 0.066. Thus it will be seen that the tile had excellent resistance to kerosene, vegetable oils, and to alkalis.

#### Example 5.

To 150 parts of water containing, by weight, 6 parts Dresinate 214 (a disproportionated rosin soap designed for use as a solvent in emulsion polymerization), 93 parts of monomeric styrene and 7 parts of acrylonitrile are added. One part of benzoyl peroxide is then added, and the mixture stirred at 70°C for 24 hours. The polymer is precipitated by the addition of alcohol and dried. 52 parts of the dry copolymer are mixed and plasticized with 24 parts of Aromatic Plasticizer 25 (an alkylated aromatic hydrocarbon resin of 25°C softening point) and Piccolastic A-25 (a soft polymer of styrene). This mixture melts at 105°C, and when blended in the ratio of 88 parts of the above mixture with 12 parts of Aromatic Plasticizer 25 and one part of Methox (a phthalate ester plasticizer) as plasticizers it produces a tile binder having a softening point of about 93°C. When this binder is blended in the ratios 23 parts of binder to 100 parts of filler, a greaseproof tile of initial penetration of 10 mils results, having excel-

lent resistance to kerosene, cottonseed oil, and trisodiumphosphate solution.

The resins of this invention are useful as such in the production of mastic tile but also may be used to confer their desirable properties of resistance to mineral and vegetable oils and alkali upon other binders. In this way more costly binders, such as vinyl chloride resins, may be extended while attaining in addition to economic factors the properties that characterize the invention.

As indicated above, tile having satisfactory greaseproof properties may be made also in accordance with this invention from tile resins produced from styrene copolymerized with acrylamide or methyl vinyl ketone. As to acrylamide, it has been found that copolymers with styrene containing as little as one per cent of the amide produce a tile resin that suitably plasticized and compounded with the usual tile constituents gives tile meeting the specifications for resistance to grease and alkali.

Acrylamide is not fully soluble in hydrocarbon diluents but is soluble in ketones which dissolve both the monomer and the copolymer to insure homogeneous reaction.

#### Example 6.

As an example, 97 parts of styrene were refluxed with three parts of acrylamide in cyclohexanone as solvent at 140° to 150°C during 48 hours. Upon evaporation of the solvent there was recovered a high melting copolymer; 58 parts of this copolymer were blended and plasticized with 42 parts of Piccolastic A-25 to produce a tile resin of 114°C melting point. This tile resin was further plasticized with 25 parts of Aromatic Plasticizer 25 (a viscous alkylated aromatic hydrocarbon resin) to provide a tile binder of 82°C melting point. 23 parts of this binder were compounded with asbestos, limestone and pigments and formed into tile which when tested showed excellent resistance to kerosene, cottonseed oil, and trisodiumphosphate solutions.

#### Example 7.

In another instance 99 parts of 99.6 per cent pure styrene monomer and one part of acrylamide were copolymerized in the same manner as in the preceding example:— Fifty-eight parts of the styrene-acrylamide resin were blended with 42 parts of Piccolastic A-25 as plasticizer to give a resin blend of 112°C softening point. Eighty-eight parts of this resin blend were plasticized with 12 parts of Aromatic Plasticizer 25 to give a tile binder of about 101°C softening point. 23.5 parts of the tile binder were mixed with 76.5 parts of asbestos fibre, limestone and pigment to provide tiles with acceptable resistance to kerosene, cottonseed oil and trisodiumphosphate solution.

The useful ranges of such copolymers of styrene and acrylamide varies between 1 per

cent and 5 or 7 per cent of acrylamide.

**Example 8.**

In the case of methyl vinyl ketone, no special technique is required, for mixtures of styrene and methyl vinyl ketone polymerize readily at 140° to 150°C using a hydrocarbon solvent, such as Hi Solv 30, to yield a clear solution. Evaporation of the solvent gives a clear high-melting point polymer that can be converted into a satisfactory tile binder by procedures such as those indicated above. This binder likewise is productive of satisfactorily greaseproof tile. In preparing the tile binder, 60 parts of the styrene-methyl vinyl ketone copolymer were blended with 40 parts of Piccolastic A-25 as plasticizer to give a resin blend of 105°C melting point. Eighty-eight parts of this resin blend were plasticized with 12 parts of Aromatic Plasticizer 25 to give a tile binder having a softening point of about 95°C. The tile binder and filler were used to produce tile with the proportions of tile binder and filler being the same as in Example 7. Copolymers of styrene with from 3 to 10 per cent of methyl vinyl ketone suffice for the purposes of this invention.

All proportions referred to hereinabove are in parts by weight. The melting or softening points stated are as determined by the Ball-and-Ring method well known in the resin art.

**WHAT WE CLAIM IS:—**

1. A resin composition for mastic tile comprising a blend of a copolymer of a major proportion of styrene and a minor proportion of acrylonitrile, acrylamide or methyl vinyl ketone, and a substantially non-volatile plasticizer, said resin having a melt-

ing point of from 70° to 110°C.

2. A resin according to Claim 1, said copolymer being one of styrene and 5 to 10 per cent of acrylonitrile.

3. A resin according to Claim 1, said copolymer being one of styrene and 1 to 7 per cent of acrylamide.

4. A resin according to Claim 1, said copolymer being one of styrene and 3 to 10 per cent of methyl vinyl ketone.

5. Mastic tile of good color stability and grease resistance, which comprises fibrous material, filler, pigment, and a thermoplastic binder, said thermoplastic binder comprising a blend of a copolymer of a major proportion of styrene and a minor proportion of acrylonitrile, acrylamide or methyl vinyl ketone, and a substantially non-volatile plasticizer, and said thermoplastic binder having a melting point of from 70° to 110°C.

6. Tile according to Claim 5, said copolymer being one of styrene and 5 to 10 per cent of acrylonitrile.

7. Tile according to Claim 5, said copolymer being one of styrene and 1 to 7 per cent of acrylamide.

8. Tile according to Claim 5, said copolymer being one of styrene and 3 to 10 per cent of methyl vinyl ketone.

9. A resin composition for mastic tile substantially as hereinbefore described.

10. Mastic tile substantially as hereinbefore described.

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